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MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

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Propellant Research and Development Division
Aerojet-General Corporation
Sacramento, California

Quarterly Technical Report AFRPL-TR-67-228

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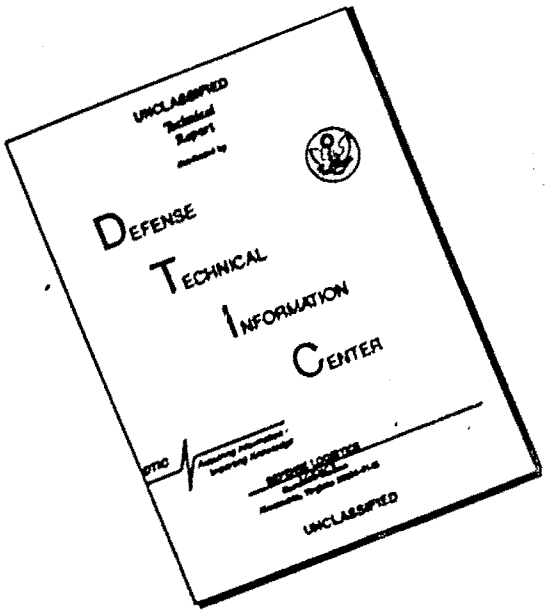

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AFRPL-TR-67-228

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

J. L. McGurk and A. J. DiMilo

FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11637 as partial fulfillment of the requirements of Project No. 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work was performed in the Advanced Propellants Department of the Propellant Research and Development Division, Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1082-81Q-4 and covers the progress made in the period 1 May to 31 July 1967. This project was monitored by Lt. Robert Bargmeyer, 1/Lt., USAF/RPCS.

The following personnel have contributed materially to the work performed during this period at Aerojet-General Corporation: H. Moe, Chemistry Specialist, J. T. Becerril, Senior Laboratory Technician, and W. Hartmann, Hawk Projects.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
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ABSTRACT

The microscopic planimetric analysis of the model grains aged six months and sectioning and sampling of a 6½ year old Hawk Motor were conducted during this quarter. For the model grains, reaction site volume-aging temperature curves after six months were different from those after three months. This may make possible the calculation of a rate constant and activation energy for the reaction occurring in this formulation for comparison with similar parameters for the reactions observed in other formulations. It also allows the investigation of the reaction under controlled conditions by introducing variables in the formulation and storage environments, and preselecting temperatures and sampling periods that will yield information of the specific reactions which occur.

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

I. INTRODUCTION

This is the fourth Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11637. The report covers the period 1 May to 31 July 1967.

The objectives of this study are to determine the course of the chemical aging process or processes in solid propellant formulations and to define the effects of these degradative chemical processes on the mechanical and ballistic properties of the propellant.

In accordance with these general objectives, the studies have been divided into two phases. The objectives in Phase I are to determine the structure, size and distribution of microscopic reaction sites in solid propellants as a function of age, formulation and storage environments; and to optically characterize and chemically analyze the reaction intermediates and products. In Phase II the mechanistic course of the aging process will be defined.

Work during the fourth quarter consisted of acquiring samples from full-scale, field-aged motors, monitoring changes in model grains, optical microscopic studies, and chemical studies.

II. PROPELLANTS UNDER STUDY

The field-aged propellants on hand are reviewed in Table I. The age reported is that at the time of sampling, because little change can be detected in small (50-gm) propellant samples or thin sections after several years storage. The 6½ year old Hawk Motor was obtained through the courtesy of Hawk projects during this quarter and cut into several sections.

The model grains under study were tabulated in the previous quarterly report (AFRPL-TR-67-136). Samples taken from these grains after nine months of aging were microtomed and mounted on microscope slides for study during the next quarter. The model grains were returned to their respective storage environments.

Table I

REVIEW OF PROPELLANTS UNDER STUDY

Motor	Amount, lb	Age[a] Years	Year Sampled
Hawk 09692 or (594)	¼	3½	1964
Hawk 08084	5	4½	1965
Hawk 15121	150	5½	1966
Hawk 09708	150	6½	1967
Minuteman 76014	80	3	1967
Minuteman Igniter	< 1/4	1	1966
Polaris Cycling Unit	80	5½	1964
Polaris Cycling Unit	30	7½	1966

[a]At time of sampling.

III. OPTICAL AND MICROSCOPIC STUDIES

A. MICROSCOPIC REACTION SITES

1. General

During this quarter microscopic studies continued on characterization and volumetric determination of the refractive type sites. The colored sites illustrated and discussed in the previous report do not have sufficiently sharp boundaries to attempt a microscopic volumetric measurement; consequently, chemical methods are being applied to determine possible concentration gradients.

2. Refractive Type Reaction Sites

Some general characteristics of refractive type sites were illustrated in the second Quarterly Report (AFRPL-TR-67-41, pages 6-7, Figures 1a, 1b, 2a and 2b). At the time, no mechanism for the formation of the clear halo shown in Figures 1a and 1b or of the surface swelling in Figures 2a and 2b was suggested. It was concluded from the map data in the third Quarterly

Report (AFRPL-TR-67-136) that a liquid phase within the grain was migrating to cause the concentration gradient. If this migrating material reacted and built up the clear halo around the aluminum, there should be indications of what happened to the original propellant around the site. The area around the site could not be seen in the previous igniter photomicrographs because of the high density of opaque solids surrounding unaltered propellant matrix. To overcome this difficulty, a propellant was obtained with a formulation similar to the model igniter and which could be microtomed considerably thinner. The photomicrographs of this propellant (Figures 1a and b of this report) show that a ring of opaque solids has collected outside the clear area of the reaction site. The aluminum particles in Figure 2a and higher magnification in Figure 2b represent a slightly different state in the reaction. The aluminum has been corroded away until only a very fine network of aluminum mesh is seen. At other reaction sites, such as in Figure 1, the aluminum surface is highly serrated, indicating surface corrosion. Thus, the external opaque ring probably includes copper chromite (CuO2O2) and aluminum that was pushed aside plus some corrosion fragments of the large central aluminum. To investigate possible reasons for the variable corrosion process, aluminum particles were embedded in an epoxy, polished and etched. In Figure 3, a large single aluminum particle is shown to consist of multiple grains. In general, some particles are composed of a few grains while others are multigranular and it is probable that surface corrosion occurs where the particle has a few grains and the network corrosive process occurs on those with the multiple grain structure. The fine aluminum particles were observed to be mostly single grains. As shown in Figure 3, there appear to be numerous impurities within the aluminum particle which are exposed by the reaction.

A refractive type reaction site from the igniter model grain aged six months is shown in Figure 4 in four types of transmitted light at the same magnification; a) intense convergent light which shows the lack of opaque material, b) plane parallel light which shows the multiple phase composition of transparent material, c) dark field phase which shows the altered refractive index of the transparent material, and d) doubly polarized light which shows the presence of several birefringent crystals, which should be fine ammonium perchlorate. Thus, the reaction halo contains little NH_4ClO_4 as well as metallic solids. Numerous variations of these refractive sites occur; some are very clear and others complex, but most have a well defined boundary which permits an estimate of their area with a grid eyepiece. One unusual variation is shown in Figures 5a and 5b at two magnifications. In Figure 5a the refractive site is the small, round, clear area left of the large black aluminum particle and below the large white angular NH_4ClO_4 crystal. At higher magnification (Figure 5b) a dendritic structure of opaque solids is seen in the right side of the refractive site. A well defined dendrite is usually indicative of precipitation and crystallization. The opaqueness and the environment suggest a metallic sulfide but not an aluminum oxide, which would be transparent.

3. Genesis of a Refractive Site in the Model Igniter Grain

The observations to date would suggest that the refractive sites are formed by outward migration of a volatile component that leads to a reaction with selected aluminum particles. The aluminum reaction may indicate a slightly basic environment which would favor the attack on the aluminum oxide coating. On the other hand, an acid environment will readily attack the aluminum along its grain boundaries. Some of the ammonium perchlorate crystals apparently dissolve and some seem to react in the solid state to form ammonium chloride. A reaction with the binder first breaks it (the binder) down sufficiently to permit redistribution of one to five micron size particles, and subsequently, a different binder reaction produces a new polymer with a considerably different refractive index.

4. Planimetric Analysis of Refractive Sites in Model Igniter Grains Aged Six Months

In the previous Quarterly Report the procedures used for planimetric analysis of reaction site concentrations were described and applied to samples aged three months. The only change in the procedure has been to maintain the isopleth interval a uniform 6% with the initial isopleth at 3%. The analysis of the six-month samples has been limited to the ray tips. The samples are further designated by a letter that indicates their axial distance from the end of a grain; A samples being $1\frac{1}{2}$ inches and B samples, $2\frac{1}{2}$ inches from the end. Figures 6, 7, 8, and 9 are isoplethic maps (volume concentration contours) which express the relative concentration gradients. Maps of the grain aged at 110°F are in both Positions A and B, while the others are in the B position. The 120/50°F sample was stored for the first 3 months at 120°F and the next 3 months at 50°F. The results of the planimetric analyses for the 3- and 6-month periods are shown in Table II and Figure 10. It is apparent that the formation or growth of refractive type reaction sites has continued during the 3- to 6-month interval, but at a reduced rate from the first three-month interval. Whether the difference between the 110A and B samples is due to propellant variation (one thin section is not a random propellant sample), or a possible axial gradient is unknown. Whether the volume concentration of reaction sites has increased because of the formation of new sites or because of growth of old sites was not determined. The percent increase between the 3- and 6-month periods is shown in Figure 11. The lower position of the 120°F point reflects a possible retardation of the reaction by the 50°F storage for part of the interval. At least, the point is about at a position of the maximum cumulative error; if the same retardation is found in the 9-month sample, it is probable that 50°F storage is on the other side of a bell-shaped curve (Figure 10). A bell curve is indicated on the basis that the reaction can be stopped by storage at high (180°F) temperature and by storage at some lower unknown temperature.

Table II

RELATIVE VOLUME PERCENT OF REFRACTIVE SITES IN MODEL IGNITER AGED FOR 3 and 6 MONTHS

Storage Temp (°F) and Position[a]	Aging Time, months		Volume[b] Increase, %
	3	6	
110B		52.5	38.5
110A	37.9	43.5	
120B		38.9	24.3
120A	31.3		
130B		25.0	17.9
130A	21.2		
150	5 est.		
180A	1 est.		

[a] A = 1½ inches and B = 2½ inches from end of grain.

[b] (E value at 6 months - A value at 3 months)/A value at 3 months.

5. Colored Reaction Sites in Model Bipropellant Grains

Colored reaction sites appeared in the sample aged 3 months as a gray-green diffuse precipitate; after 6 months of aging they were found throughout most of the ray section and were partially condensed into definite Liesegang Ring (actually shells) structures. In the 9-month sample the red gel center, similar to those in the 4½ and 5½ year old Hawk motors, was observed. The diffuse color boundaries do not permit a microscopic volumetric analysis and a chemical method is being devised to determine if various inorganic ions have migrated to form a concentration gradient. A microscopic frequency plot of the colored reaction sites can be prepared and, in conjunction with the chemical analysis, an isopleth map can be constructed.

The schematic map in Figure 12 illustrates recent observations on the general distribution of refractive and colored reaction sites in a small 6- to 9-month old bipropellant grain stored at 120°F.

IV. CHEMICAL STUDIES

Chemical analysis of the degraded binder from a Polaris Cycling Unit had previously revealed that the ethylene dichloride soluble material was composed of polyurethane fragments of varying molecular weights. Separation and identification was achieved by column chromatography and infrared spectroscopy, respectively. The emphasis in this quarter has been to define more accurately the chemical components and environmental conditions required to produce the high refractive index material and colored reaction sites that have been observed microscopically. A stock polyurethane binder, with a composition similar to that used in a Minuteman Igniter Propellant, was chosen as the reaction matrix. The following were added, individually and in combination: Al, NH_4ClO_4, FeAA, copper chromite and TDI. Each of these samples (ca. 5-gm size) was placed in a 110°F oven and removed and examined periodically. To date, no reactions have been observed.

The high refractive index material present in the Polaris Unit is being chemically analyzed. Because of the low solubility in common solvents and low volatility of this material, analysis by conventional techniques such as infrared and chromatography is not feasible. More polar solvents such as dimethyl sulfoxide and dimethylformamide dissolve this material, but the solvents themselves interfere with the analyses. Attempts to improve the analytical method are continuing.

A propellant sample was taken from Hawk Motor 15121 that contains the previously reported size gradient of colored reaction sites in the booster grain between bipropellant interface and bore surface. Attempts are underway to analyze any differences in FeAA concentration and total iron concentration in different zones of the propellant grain.

V. FIRST YEAR REVIEW

This program was initiated to investigate observations reported earlier[1] on the occurrence of microscopic reaction sites in five year old Polaris and four year old Hawk polyurethane propellants with the objective of gaining from these observations new knowledge on the general problem of chemical changes in propellant aging.

In considering the technical approach to attaining program objectives, the latest data shows that a significant advance in this area has been made. The proposed approach was to obtain samples where possible from sufficient field-aged motors and apply a statistical analysis to help solve the difficulties inherent in nonperiodic random sampling, complex storage histories, variable formulations, and casting time. To overcome a possible deficiency

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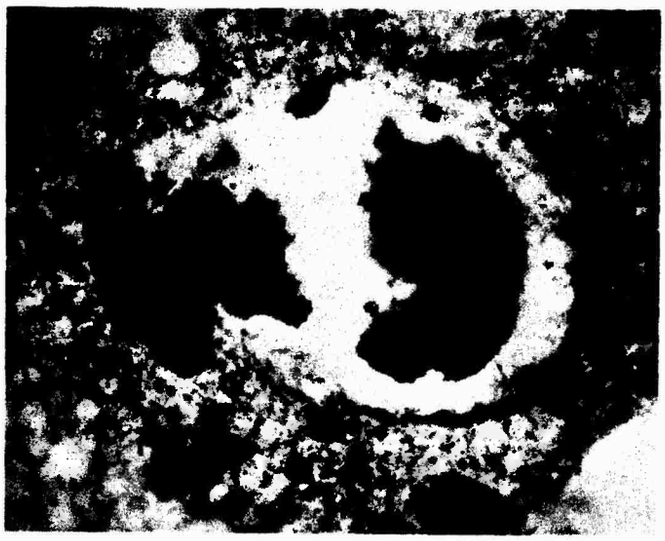
(1) J. L. McGurk, "Microscopic Determination of Near Solid State Changes in Aged Propellant", A.A.I.A. Journal, 3, 1890-95 (1965).

of field samples, model grains were cast and stored at various temperatures on the probability that at least one would be useable after some time lapse that was to be determined by periodic sampling. The data from the model grains indicated that the aging reaction occurred at most of the storage temperatures and at progressively reduced rates as the storage temperature increased. Furthermore, the changes were quantitatively measurable within the discrimination limits of the microscopic planimetric procedures at each of the selected sampling periods. As a consequence, the reaction sites can now be produced in a controlled manner, formulation variables introduced, and temperature and sampling periods preselected to be within the discriminatory limits of the volumetric procedure using the optical microscope. Thus, reaction rates can be determined for the observed processes. The reaction rates will be a significant factor in obtaining a solution to the problem of whether the rapid rate (months) in the small model grains can be extrapolated to the apparent rate (as yet unproved) of several years in the larger field motors. Reaction rates for the overall process will also permit comparison between formulations.

The reaction in model grains apparently requires a good part of a year and use of the procedure in the coming year, along with the tasks currently in progress will, at best, result in acquisition of only partial data. However, since to date, the chemical analyses have given little information on the specific chemical reactions that occur, consideration is being given to (1) preparing model grains with formula variations and (2) using the data to determing the reacting species and, thus, obtain information on the chemistry involved in the aging reactions.

REFRACTIVE SITE WITH RING OF OPAQUE SOLIDS



a

320X

b

Figure 1

REACTION OF ALUMINUM

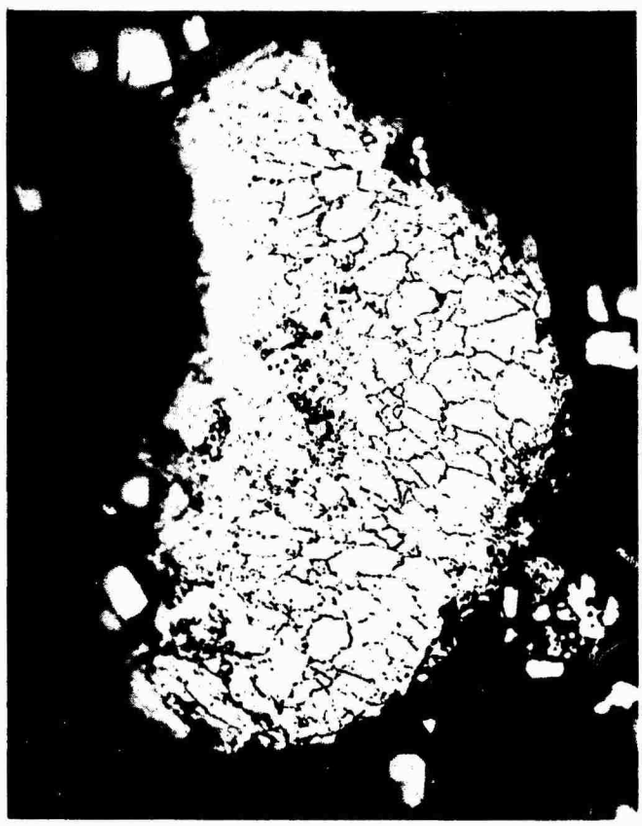
a 125X

500X

b

Figure 2

POLISHED AND ETCHED ALUMINUM PARTICLE
SHOWING GRAIN BOUNDARIES



500X

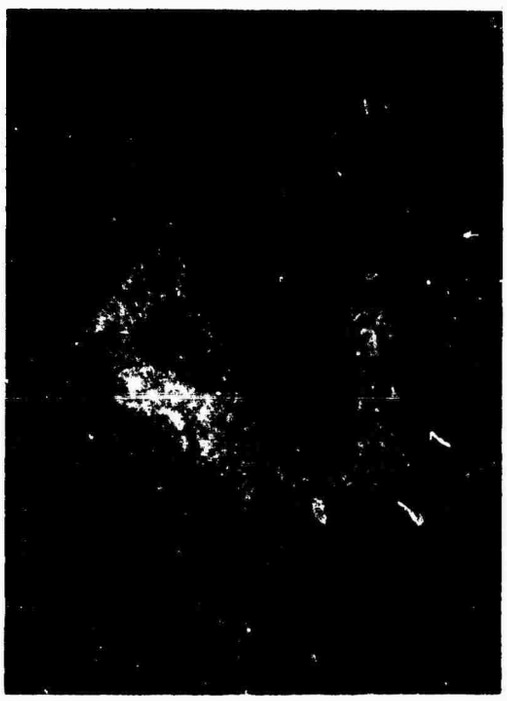
Figure 3

A REFRACTIVE SITE IN TRANSMITTED LIGHT

a. Convergent

125X

b. Plane polarized



c. Dark field

d. Doubly polarized

Figure 4

OPAQUE DENDRITES IN A REFRACTIVE SITE

a 250X

b 500X

Figure 5

ISOPLETH MAP, MODEL IGNITER GRAIN
6 Months 110°F, A

Figure 6

ISOPLETH MAP MODEL IGNITER GRAIN
6 Months 110°F, B

Figure 7

ISOPLETH MAP, MODEL IGNITER GRAIN
3/3 Months 120/50°F, B

Figure 8

ISOPLETH MAP, MODEL IGNITER GRAIN
6 Months 130°F, B

Figure 9

RELATIVE VOLUME CONCENTRATION OF REFRACTIVE SITES
IN MODEL IGNITER GRAINS AGED 3 AND 6 MONTHS

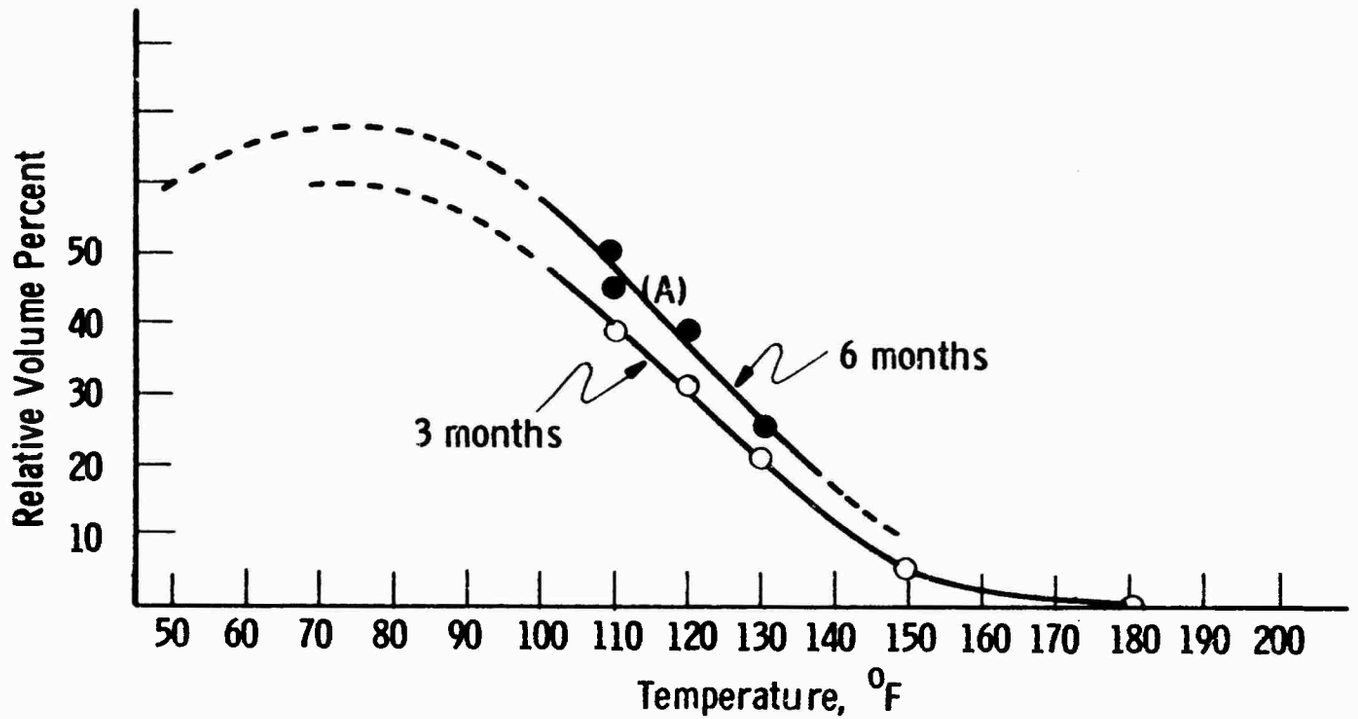


Figure 10

PERCENT INCREASE IN REACTION SITE VOLUME
BETWEEN 3 AND 6 MONTHS SAMPLES

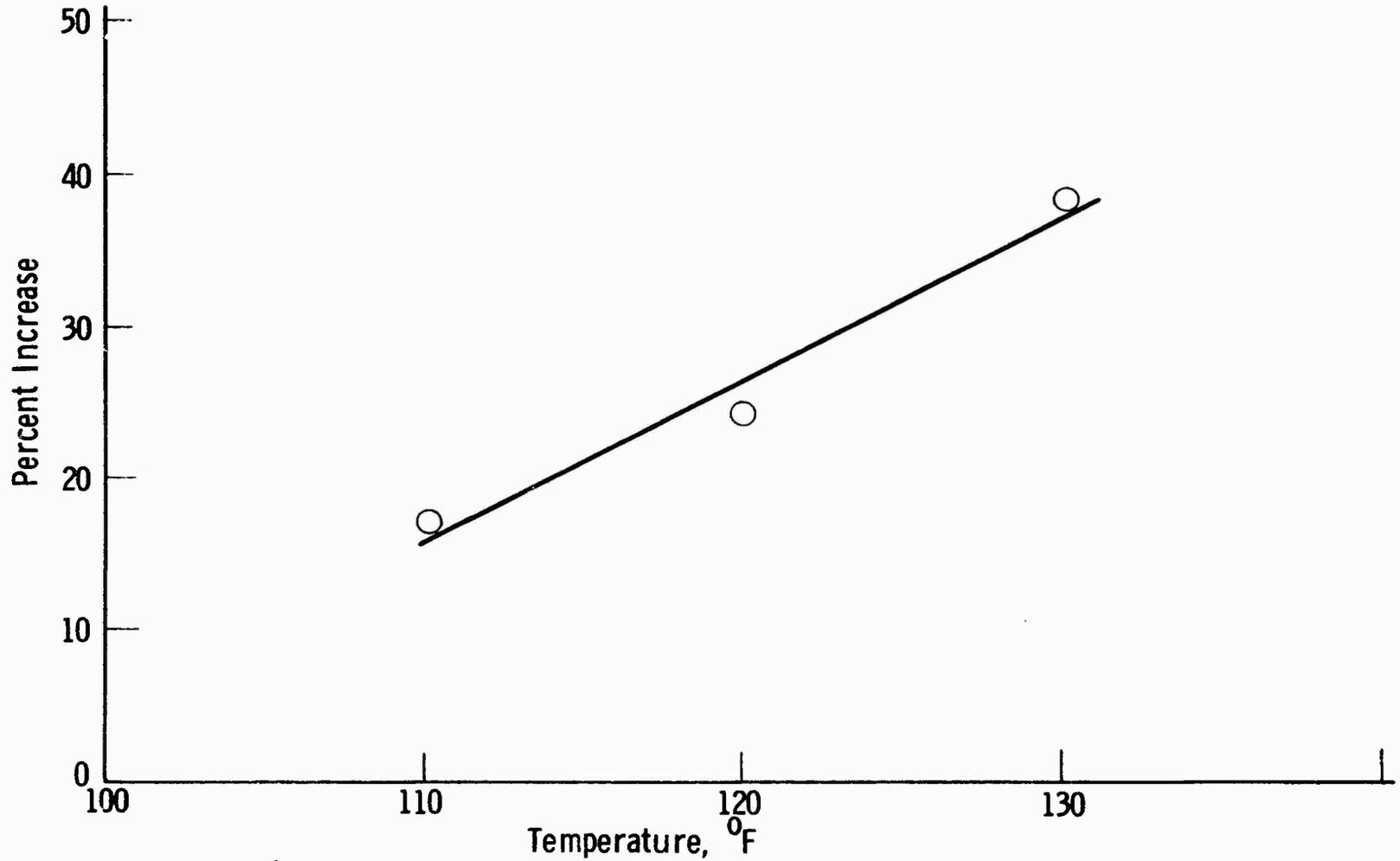


Figure 11

SCHEMATIC ISOPLETH MAP SHOWING LOCATION OF COLORED AND REFRACTIVE REACTION SITES IN A BIPROPELLANT CROSS SECTION

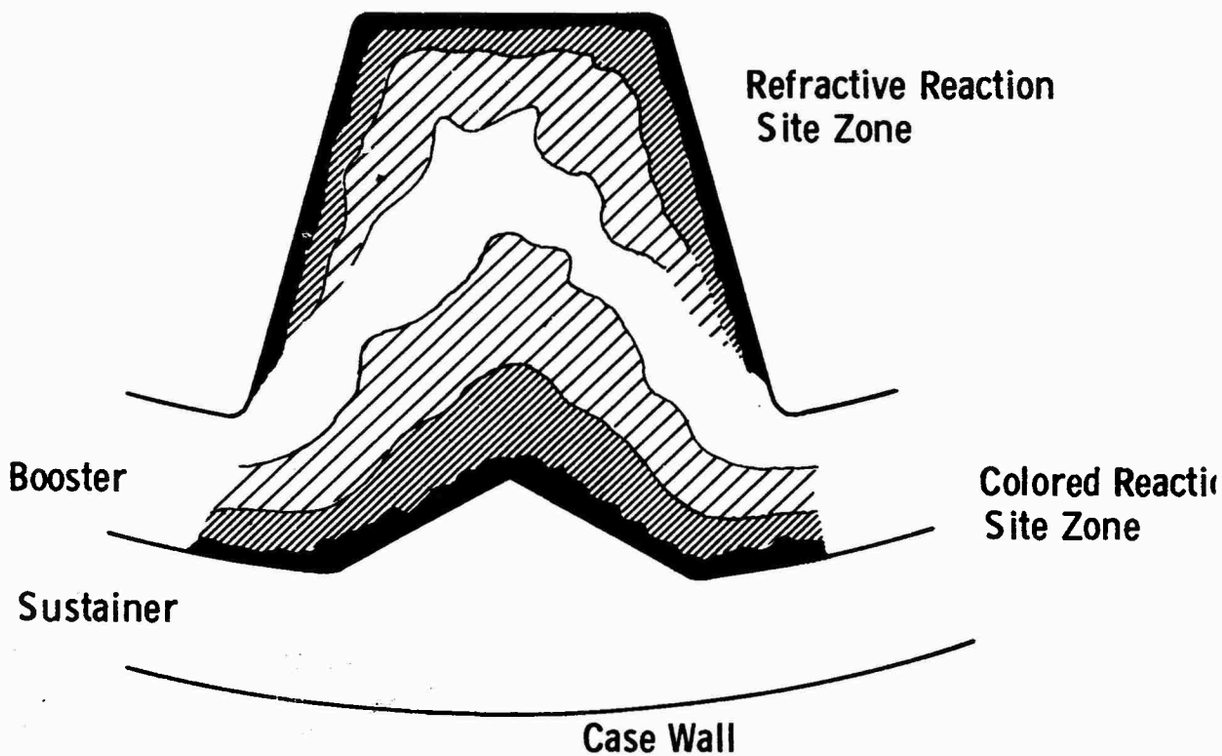


Figure 12

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